Insight — Application Note 2.10

Cure Monitoring of Carbon Fiber Reinforced Prepreg (CFRP)

Introduction

Samples from a single batch of carbon fiber reinforced prepreg (CFRP) were tested for repeatability and effect of temperature on cure rate. The data from dielectric cure monitoring clearly show:

- Critical Points identify characteristic features of the cure such as minimum ion viscosity, maximum slope of log(ion viscosity) and the time to a chosen end of cure.
- Cure time decreases as cure temperature increases, as expected for a reaction that is thermally driven.

Definitions

This application note presents and discusses data for *log(ion viscosity)* and *slope of log(ion viscosity)*, which indicate the state of cure. The plots show characteristic features such as minimum ion viscosity, maximum slope of log(ion viscosity) and the time to a chosen end of cure. For brevity, log(ion viscosity) will be called *log(IV)* and slope of log(ion viscosity) will simply be called *slope*.

Electrical conductivity (σ) has both frequency independent (σ_{DC}) and frequency dependent (σ_{AC}) components. In an oscillating electric field, σ_{DC} arises from the flow of mobile ions while σ_{AC} arises from the rotation of stationary dipoles. These two responses act like electrical elements in parallel and are added together as expressed below:

(eq. 10.1) $$\sigma = \sigma_{DC} + \sigma_{AC} \qquad (\text{ohm}^{-1} - \text{cm}^{-1})$$

Resistivity (ρ) is the inverse of conductivity and is defined as:

(eq. 10.2) $$\rho = 1/\sigma \qquad (\text{ohm-cm})$$

From its relationship to conductivity, resistivity also has both frequency independent (ρ_{DC}) and frequency dependent (ρ_{AC}) components. Crosslink density, which is a measure of cure state, affects both mechanical viscosity and the movement of ions, and therefore influences ρ_{DC}. As a result, the term *Ion Viscosity* was coined to emphasize the relationship between mechanical viscosity and ρ_{DC}. Ion viscosity (*IV*) is defined as:

(eq. 10.3) $IV = \rho_{DC}$ (ohm-cm)

Procedure

Samples were tested using the Ceramicomb-1″ sensor, which was embedded into the lower heater platen of a press as shown in Figure 10-1. A sheet of laboratory grade filter paper was placed on top of the sensor to allow flow of resin to the sensor while preventing carbon fibers from short circuiting the electrodes. Two layers of CFRP approximately 1″ x 1″ were then placed on top of the filter paper. During each test the press applied heat and pressure to the lay-up.

An LT-451 Dielectric Cure Monitor measured dielectric properties at 100 Hz and 1.0 KHz excitation frequencies. CureView software acquired and stored the data, and performed post-analysis and presentation of the data.

CureView can extract Critical Points only for data obtained at a single frequency; therefore the first tests on a material require measurement with multiple frequencies to determine an optimum single frequency. During subsequent tests CureView can extract Critical Points automatically and characterize the cure.

Figure 10-1
Ceramicomb-1″ reusable sensor embedded in press platen

Repeatability of measurements

Figure 10-2 shows the results from one of five tests of fresh CFRP under identical conditions: temperature was 120 °C and pressure was approximately 10 psi. The minimum of the log(*IV*) curve, also the time of minimum mechanical viscosity, occurs at the start of the test. This point is called Critical Point 2 (CP(2)). Minimum viscosity occurs when the thermally driven reaction dominates the decreasing viscosity caused by "melting." At 120 °C, the reaction dominates from the very start.

Maximum slope occurs at approximately 15 minutes, indicating the time of maximum reaction rate. This point is called Critical Point 3 (CP(3)). After this time the reaction slows and the cure is in its end stage. Although some users identify CP(3) with gelation, gelation is actually a mechanical event that has no dielectric indicator. At best CP(3) may be used as a signpost *associated* with gelation but not *identifying* gelation

By the end of the test the material is still slowly curing, as indicated by the non-zero slope of log(*IV*). To define the end of cure, the user may choose a particular slope, also called Critical Point 4 (CP(4)), according to the needs of the application.

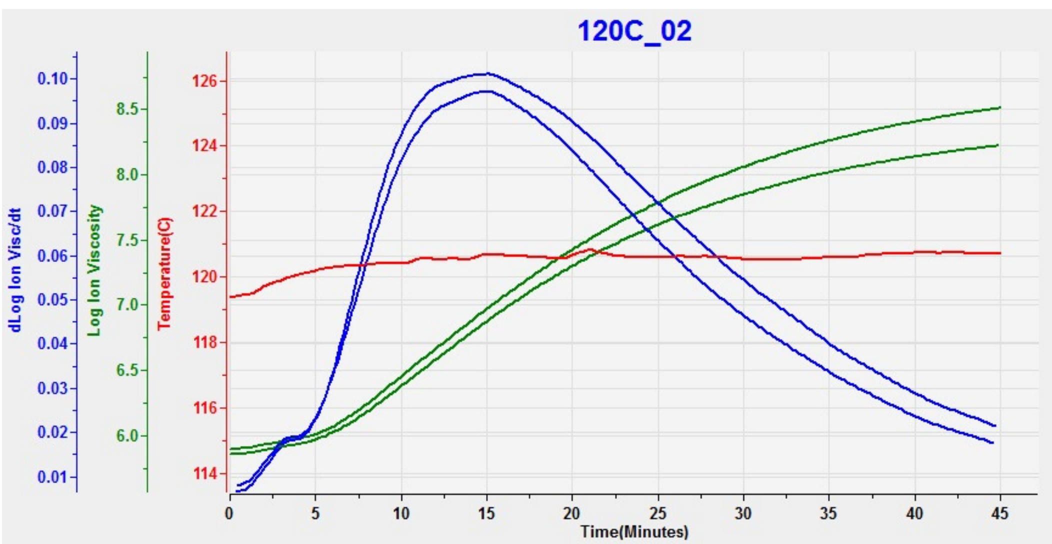

Figure 10-2
CFRP cure at 120 °C, 100 Hz and 1 kHz data

Figures 10-3 and 10-4 show log(*IV*) and slope curves for the 100 Hz data from six tests. The data are overlaid on top of each other to reveal typical reproducibility and range of variation.

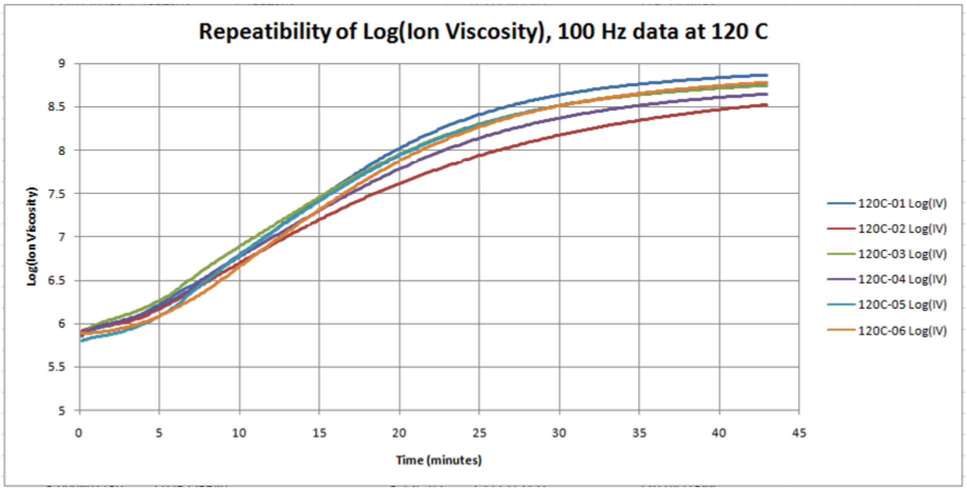

Figure 10-3
Log(IV) from cures of six samples of CFRP

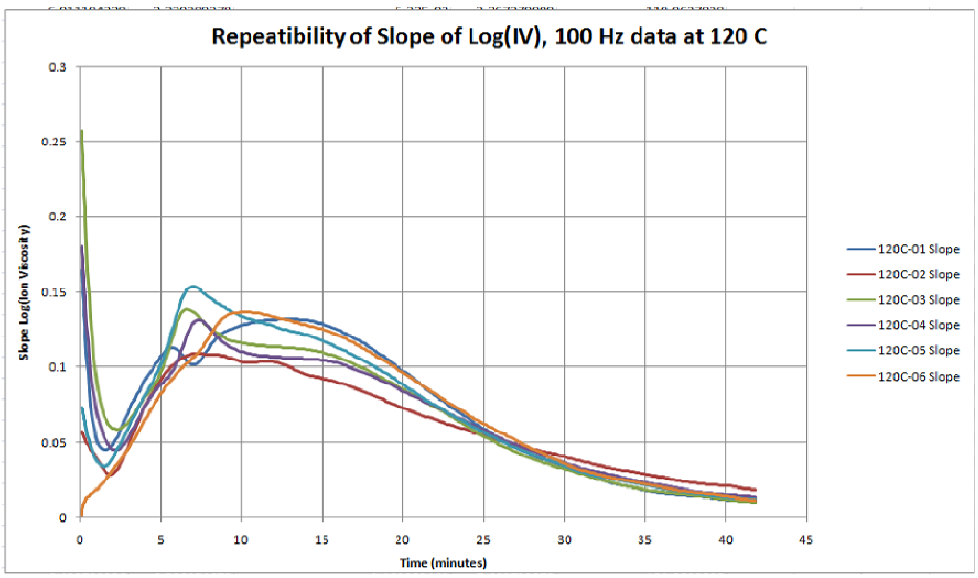

Figure 10-4
Slope from cures of six samples of CFRP

Effect of process temperature on cure rate

Figures 10-5 through 10-8 show results from samples of the same fresh CFRP tested at 120 °C, 135 °C, 150 °C and 165 °C.

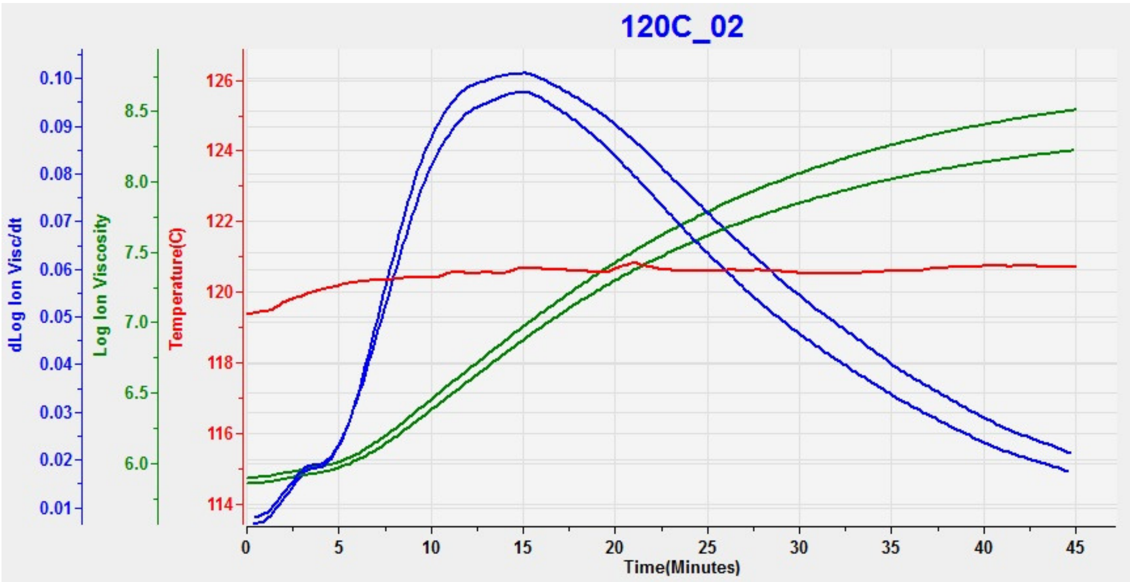

Figure 10-5
CFRP cure at 120 °C, 100 Hz and 1 kHz data

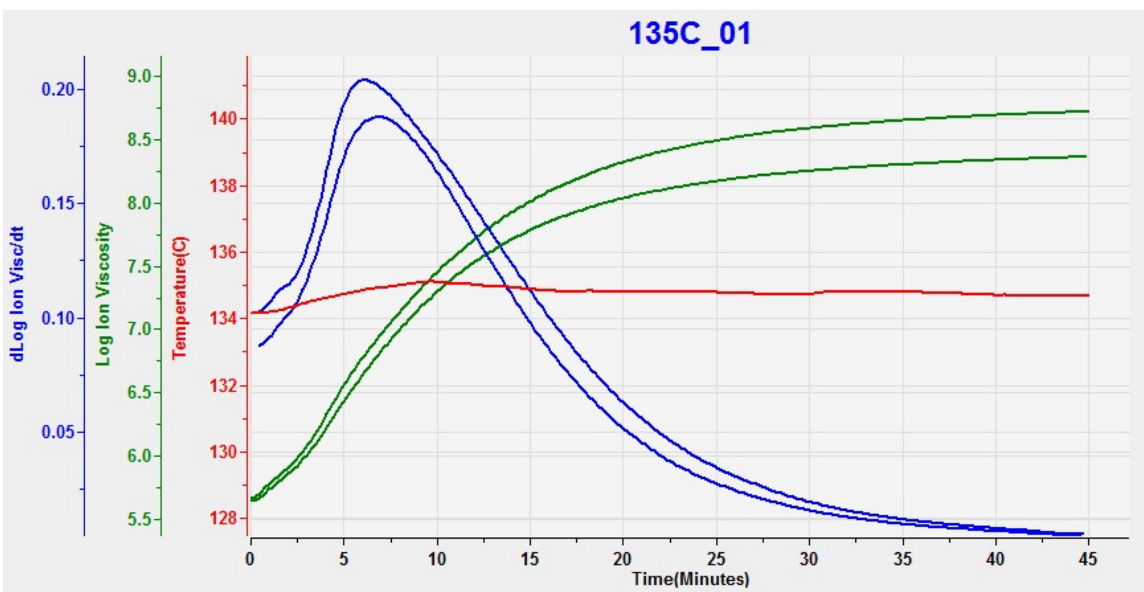

Figure 10-6
CFRP cure at 135 °C, 100 Hz and 1 kHz data

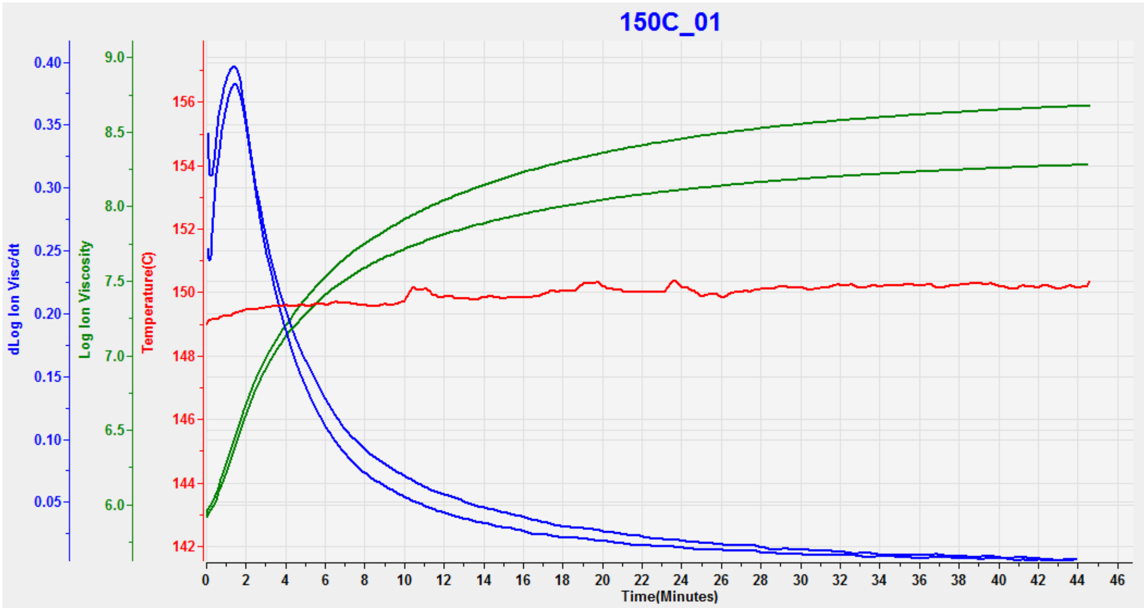

Figure 10-7
CFRP cure at 150 °C, 100 Hz and 1 kHz data

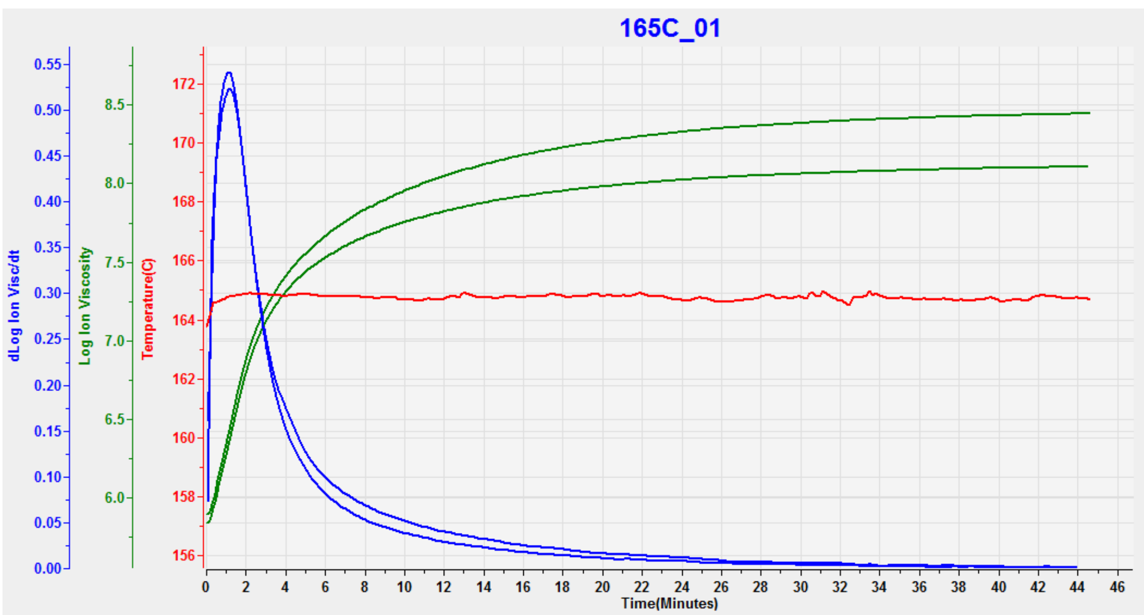

Figure 10-8
CFRP cure at 165 °C, 100 Hz and 1 kHz data

Figure 10-9 overlays log(*IV*) data for the cures at 120 °C, 135 °C, 150 °C and 165 °C. Figure 10-10 overlays slope data for these cures. As expected, higher processing temperatures result in faster cures, but the use of Critical points is necessary to quantify this relationship.

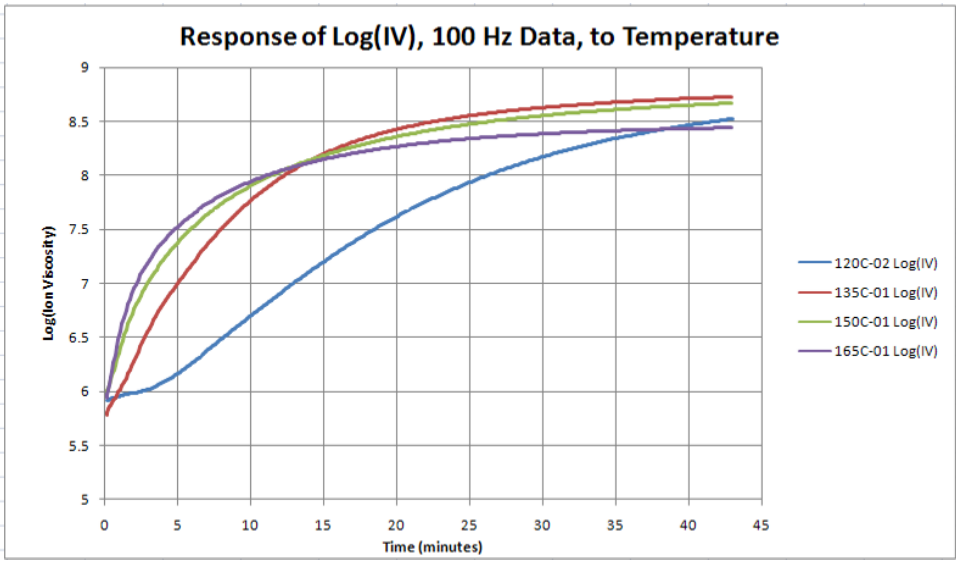

Figure 10-9
Log(*IV*) curves from isothermal cures at different temperatures

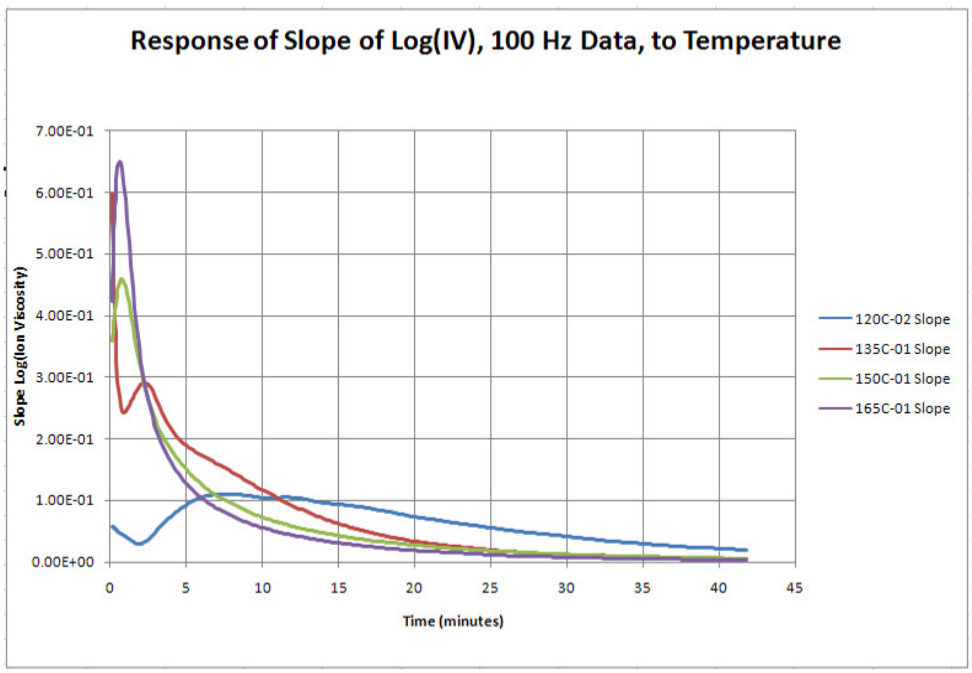

Figure 10-10
Slope curves from isothermal cures at different temperatures

Table 1 shows values for the time to reach maximum slope—CP(3)—and the level of this slope. The time to CP(3) should decrease with higher temperature because the reaction rate is faster. The level of CP(3) indicates the maximum reaction rate and both should increase with higher cure temperature.

Table 1 also shows the time to reach the end of cure—CP(4). For purposes of this analysis, a slope of 5.00 E-2 was arbitrarily chosen, but in practice the user must determine the slope to indicate end of cure based on the needs of the application. As expected, the time to reach CP(4) decreases as cure temperature increases.

Table 10-1
Effect of temperature on Critical Points

Cure Temp. (℃)	CP(1) Crit. Visc.		CP(2) Min. Visc.		CP(3) Max Slope		CP(4) Crit. Slope	
	Value	Time (min)	Value	Time (min)	Value	Time (min)	Value	Time (min)
120	---	---	---	---	8.96E-02	7.282	5.00E-02	26.453
135	---	---	---	---	2.90E-01	2.314	5.00E-02	16.603
150	---	---	---	---	4.58E-01	0.782	5.00E-02	13.612
165	---	---		---	6.50E-01	0.576	5.00E-02	11.970

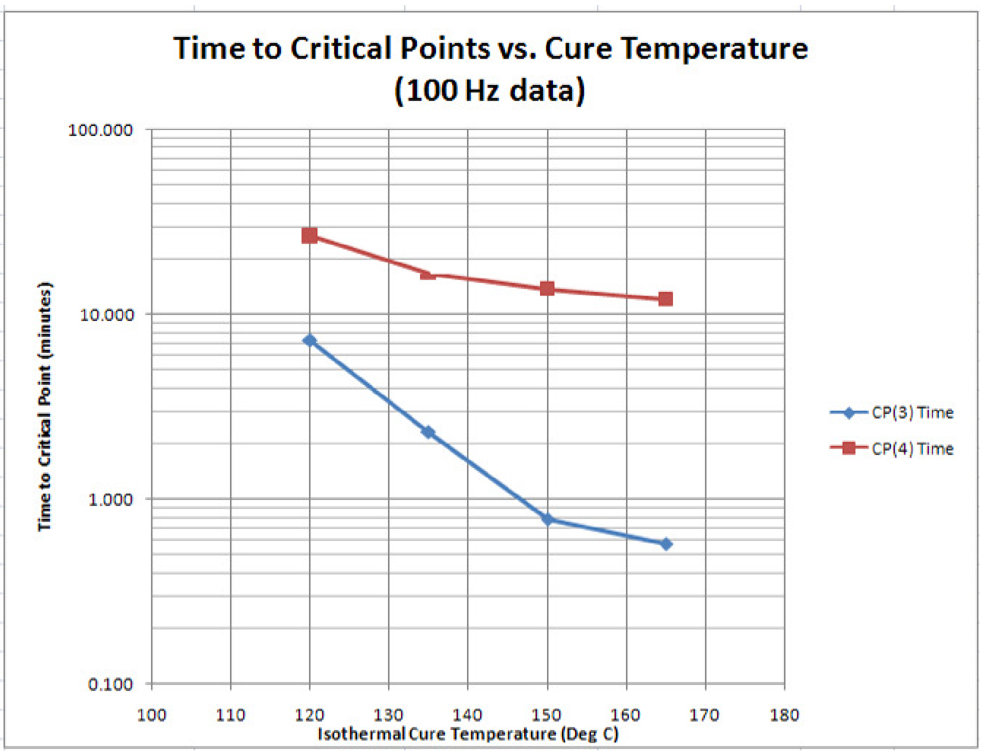

Figure 10-11
Time to Critical Points 3 and 4 vs. cure temperature

Figure 10-11 plots the time to CP(3) and CP(4), and shows how they decease with increasing cure temperature. In particular, note how the time to CP(3), the time to the point of maximum reaction rate, decreases exponentially with an increase in temperature. This indicates an Arrhenius relationship between reaction rate and temperature. The CP(3) data point at 165 °C deviates from a straight trend line of the lower temperatures, possibly because of limited accuracy in identifying CP(3) times that are less than one minute.

Figure 10-12 shows the level of CP(3)—the level of maximum slope—which indicates maximum reaction rate. Like the time to CP(3), the level of CP(3) shows an Arrhenius relationship with temperature. The data at 165 °C may depart from a straight trend line because of limitations in measurement accuracy for the fast reaction.

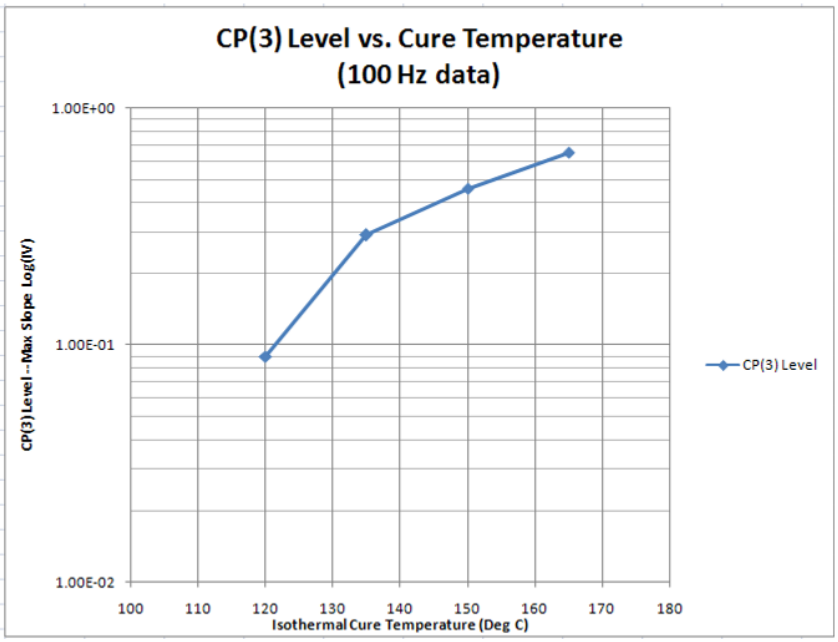

Figure 10-12
CP(3) level vs. cure temperature

Figure 10-13 plots the level of CP(3) vs. the time to reach CP(3). Accounting for measurement accuracy, the level of CP(3) increases exponentially with temperature while the time to CP(3) decreases exponentially with temperature.

Characteristics of a thermoset Cure

Ion viscosity is defined as the frequency independent resistivity, ρ_{DC}. In many cases ion viscosity is proportional to mechanical viscosity during the early portion of cure, and indicates cure state in the latter portion of cure.

Ion viscosity derived from data at a single frequency produces a curve that characterizes the progress of cure. In simplified form, Figures 10-13 and 10-14 show the behavior of a typical thermoset with one temperature ramp step and one temperature hold step.

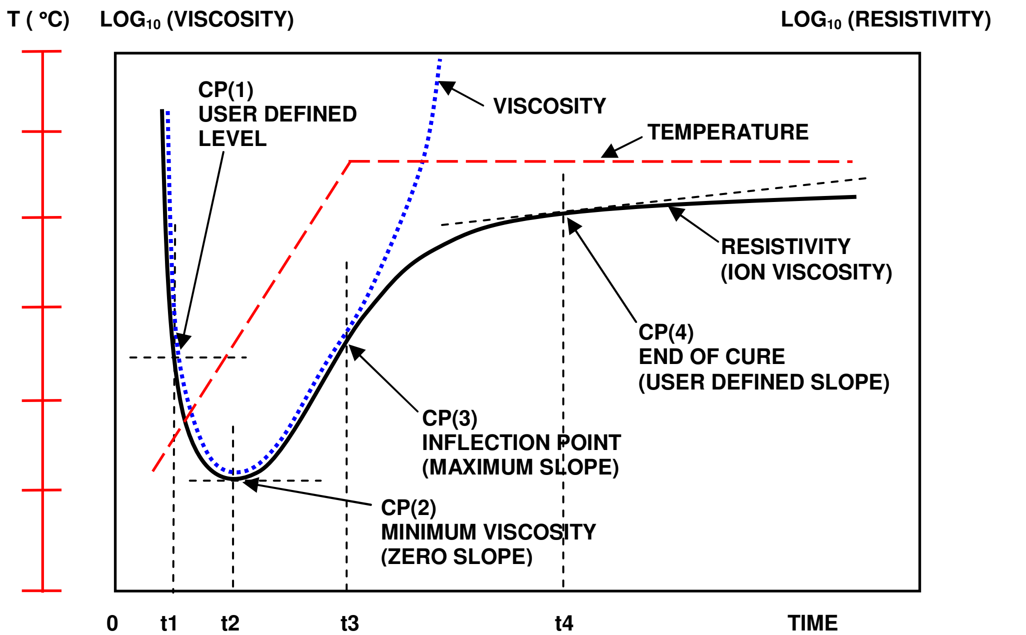

Figure 10-13
Typical ion viscosity behavior of a curing thermoset

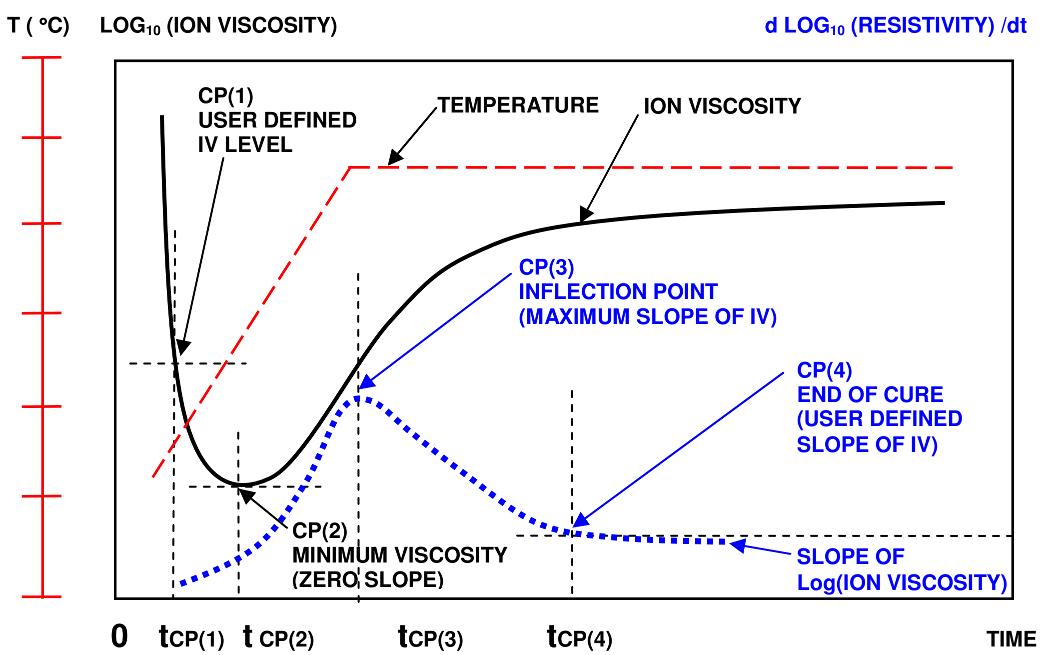

Figure 10-14
Ion viscosity curve and slope of ion viscosity of a curing thermoset

At first, as temperature increases, ion viscosity decreases because the thermoset is melting, becoming more fluid and therefore less resistive. The reaction rate increases as the material becomes hotter. At some time the increase in ion viscosity due to crosslinking overcomes the decrease in ion viscosity due to increasing temperature. This point is the ion viscosity minimum, which also occurs at the time of minimum mechanical viscosity.

After the minimum point, ion viscosity increases continuously until the concentration of unreacted monomers diminishes and the reaction rate decreases; consequently the slope of ion viscosity also decreases and eventually ion viscosity will have zero slope when cure has stopped completely.

Four Critical Points characterize the dielectric cure curve:

- CP(1)—A user defined level of ion viscosity that is typically used to identify the onset of material flow at the beginning of cure.
- CP(2)—Ion viscosity minimum, which typically also corresponds to the physical viscosity minimum. This Critical Point indicates the time when the crosslinking reaction and resulting increasing viscosity begins to dominate the decreasing viscosity due to melting.
- CP(3)—Inflection point, which identifies the time when the crosslinking reaction begins to slow. CP(3) is often used as a signpost that can be associated with gelation.
- CP(4)—A user defined slope that can define the end of cure. The decreasing slope corresponds to the decreasing reaction rate. Note that dielectric cure monitoring continues to reveal changes in the evolving material past the point when mechanical measurement of viscosity is not possible.

Conclusion

Dielectric measurements allow observation of the cure of thermosets in real time, and the extraction of Critical Points quantify the characteristics of the reaction. The carbon reinforced prepreg data of this report show that results are repeatable and consistent from sensor to sensor. Dielectric cure monitoring over temperatures from 120 °C to 165 °C clearly indicate the direct correlation between temperature and rate of cure.

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